Effect of Some Molecular Structural Factors on the Mechanical Properties of Polyvinyl Alcohol (Special Issue on Polymer Chemistry, I)

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The effects of residual acetyl content, molecular weight and its distribution of polyvinyl alcohol (PVA) on some mechanical properties of its film or fiber were studied. Some unfavorable effects of the very small quantity (less than 0.5 mole %) of acetyl residue on the drawability at high temperature and tensile strength of PVA film or fiber were observed.

The linear relationship between the tensile strength of maximum stretched film of well fractionated PVA and the reciprocal value of the degree of polymerization was recognized, while such fairly linear relationship could not be recognized for unstretched film or stretched one to some lesser degree.

Examining the effect of molecular weight distribution on the mechanical properties of PVA, it was confirmed that tensile properties generally decreased with lowering number average molecular weight or with increasing inhomogeneity of molecular weight distribution even if the samples had an equal viscosity average molecular weight and were tested at an equal degree of stretching.

1. INTRODUCTION

It is most important in both scientific and practical point of view to clarify the relationship between molecular structure and mechanical properties of high polymeric materials. Especially, the relationship between molecular structure and the tensile properties of films or fibers is important for practical application. Thus, the subject has been investigated by many workers, but there still remain many problems unsolved. For instance, the mechanical properties of high polymers generally increase with increase of the molecular weight (M), but many investigators have found with various polymers that their mechanical properties behave as a constant independent of M beyond a critical value of M.

The following equation has been proposed for the relation between the mechanical properties (F) and molecular weight (M) of polymers.

$$F = a - b/M \qquad (1)$$

where a and b are constant. Equation (1) well adapts in some cases to the mechanical properties such as tensile strength, but its applicable range is limited and its theoretical base is incomplete. One of the problems is what kind of average value should be used for M in the equation (1), since any polymer usually has a wide distribution of M.

Flory[1] suggested to use the number average molecular weight (M_n), but

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it seems that there are many cases that equation (1) does not fit if the value of M_n is used. Mc Comick et al[2] synthesized some samples of polystyrene which have different distrubution of M and, by studying their mechanical properties, they suggested that a certain mean value between M_n and weight average molecular weight (M_w) should be taken as the value of M in the equation (1).

To ascertain this problem experimentally, it is necessary to prepare many polymer fractions which have different average M and a very narrow distribution, or many polymer homologues of known distribution. This kind of works is very troublesome. Mc Comick et al[2] used polystyrene which was obtained by anionic polymerization and had very high homogeneity of M, so they were able to get well-regulated data. But so far as we are aware, satisfactory results have not been obtained yet for other species of polymers, though many investigations have been continuously made on this subject.
Thus there remains many unsolved problems even if only the molecular weight or its distribution is concerned as the molecular structural factor. The object of this work is to clarify the effects of mclecular weight and its distribution on mechanical properties of PVA film or fiber. The effect of a small quantity of acetyl residue in PVA was also studied.

2. EXPERIMENTAL

2.1. Polyvinyl Alcohol (PVA)

Commercial grade PVA was used and resaponified to decrease its acetyl content below 0.1 mole% except in the case of studying the effect of acetyl residue.

Determination of degree of polymerization (P) of PVA. PVA, after removal of sodium acetate by the extraction with methanol, was dissolved in water, and the viscosity was measured by Ostwald viscosimeter at 30±0.1°C, and P was calculated from intrinsic viscosity $[\eta]$ by using Nakajima's equation.[3]

$$[\eta]=7.50\times10^{-4}\cdot P^{0.64}$$

Determination of P of Polyvinyl acetate (PVAc). By measuring the $[\eta]$ of the acetone solution at 30±0.1° C, P was calculated using Nakajima's eqation.[4]

$$[\eta]=0.94\times10^{-4}\cdot P^{0.62}$$

Determination of residual acetyl content. About 3 g of dry PVA, extracted sufficiently with methanol, was accurately weighed into the 200 ml Erlenmayer flask, and 100 ml of distillated water was added. The solution was warmed until PVA dissolved. 25 ml of N/10 NaOH was then added into the solution, and after one day, 25 ml of N/10 sulphuric acid was added. Then excess sulphuric acid was titrated by N/10 NaOH.

Acetyl content (weight%) $\quad x=0.60\ (a-b)f/w$

Acetyl content (mole %) $y=44.05\ x/(60.05-0.42x)$

where, a : ml of titration, b : ml of blank titration, w : weight of sample (g), f : factor of the N/10 NaOH.

Resaponification of PVA. About 15 % excess of N/10 NaOH was added to 8—10 % aqueous solution of PVA, and after keeping one day at room temperature PVA thus obtained was extracted with methanol.

2.2. Preparation of PVA Film

About 4 % PVA aqueous solution was spread over on the glass plate and after drying for one night at 20—30°C film of 15—20μ thickness was obtained. The thickness of the film was calculated from the weight and area of film assuming the specific gravity of PVA was 1.28.

2.3. Preparation of PVA Fiber

PVA fiber was obtained by wet spinning using 15 % PVA aqueous solution and saturated sodium sulphate coagulation bath. After heat stretching in 180—200°C air and heat setting in 225°C air for 200 sec, PVA fiber was reacted with formaldehyde in usual way.

2.4. Measurement of Mechanical Properties

Tensile strength, elongation, knot strength and Young's modulus were measured with K-S type Seni-meter (a single fiber tensile tester). Flexual fatigue test was carried out using Franz-Henning type tester. In addition to these measurements, as a special test heat drawablity was measured at 180—200°C.

3. EXPERIMENTAL RESULTS

3.1. The Effect of Acetyl Residue in PVA

Generally, PVA is obtained by saponification of PVAc in methanol solution by adding sodium hydroxide or methoxide and through this reaction most of the acetyl groups in PVAc are saponified to hydroxyl groups, but ordinally there still remains a small quantity of acetyl group.

The effect of acetyl residues in PVA on the mechanical properties of PVA fiber has been studied by several authors. Sakurada and his coworker[5] recognized that tensile strength and Young's modulus increased in accordance with decreasing acetyl residues, while ultimate elongation did the reverse. These investigations were mainly concernod with the cases of relatively high value of acetyl residue, and it was concluded that the tensile properties of PVA fiber would not be influenced by acetyl residues below 0.5 mole %. But recently, in relation to the manufacturing of high tenacity Vinylon (PVA fiber) having tensile strength of 8—10 g/d, it was reported[9] that acetyl residue, even if its content was below 0.5 mole %, had unfavorable effect on fiber properties. Thus, in our work, the effect of acetyl residues on the tensile properties of PVA was first studied in the range of acetyl residues below

0.5 mole %.

Commercial grade PVA was used as original sample. Resaponification was completed without any change of viscosity average molecular weight (M_v). The values of M_v and the acetyl residues of original and resaponified PVA are :

Original PVA $M_v=1500$, Acetyl residue (mole %) = 0.46 ;
Resaponified PVA $M_v=1500$, Acetyl residue (mole %) = 0.1.

Drawability of these two PVA films at high temperature was examined because it was most important property to obtain high tensile strength. A film with 10 mm length and 1 mm width was conditioned in RH 65 % desiccator for one week, then stretched at a rate 15 %/sec at desired temperature, and the drawing ratio at breaking was taken as a measure of heat drawability. The results obtained are shown in Table 1. It was found that the value of the heat drawability could be obtained with good reproducibility if the preparation of the film, its thickness and conditions of measurements etc. were carefully regulated. From the Table 1, it was found that the maximum degree of drawability of the original PVA film (0.46 mole % acetyl residue) was less than that of resaponified one at all temperatures tested and

Table. 1. The effect of residual acetyl content on heat drawability of PVA film.

Film sample	Acetyl content (mole %)	Maximum heat drawability at various temperature[a] (Ratio to the original length)			
		170°C	180°C	190°C	200°C
Original PVA[b]	0.46	15.2	16.0	16.6	14.4
Resaponified PVA[b]	<0.1	15.4	17.3	17.7	17.1

[a] Values in Table show average value of 15 times testing.
[b] Film thickness is about 17μ.

Table 2. The effect of residual acetyl content on tensile strength and elongation of stretched and unstretched PVA films.

Sample[a]	Stretching ratio[b]	Tensile strength (kg/mm^2)	Elongation (%)
Original PVA film	1.0 (not stretched)	3.87	244
Resaponified PVA film	1.0 (not stretched)	3.75	226
Original	10.0	82.8	15.0
Resaponified	10.0	82.7	13.5
Original	15.0[c]	102.3	8.0
Resaponified	17.0[c]	126.1	12.0

[a] Residual acetyl content as described in Table 1.
[b] Stretched at 180°C.
[c] Stretched to nearly maximum ratio in Table 1.

that the optimum drawing temperature was 180°C or 190°C.

Tensile strength and elongation of the original and resaponified PVA film with or without drawing are shown in Table 2. It is seen from the table that the resaponified PVA gives higher value of tensile strength owing to its higher maximum degree of stretching, while no effect of acetyl residues is observed in the cases of the same degree of stretching. In the case of fiber which was prepared from these two PVA by wet spinning, the same results were observed. Tensile strength of 126.1 kg/mm^2 for the maximum stretched resaponified PVA film shown in Table 2 corresponds to 10.9 g/d if we assume the density of PVA is 1.28. So it is shown that high tenacity vinylon having tenacity of over 10 g/d may be obtained from the commercial grade PVA (P=1500) if complete resaponification and high stretching are given.

3.2. The Effect of Degree of Polymerization (P)

The relationship between tensile properties and molecular weight of polymers is very important for practical application, so many workers[7] had studied this subject with several polymers. However in those studies the effect of the molecular weight distribution and molecular orientation has not been considered so enough. Thus the main object of this work is to investigate this problem.

At first, PVA described above was fractionated into several fractions by using water as solvent and acetone-water as precipitant, and films were prepared using each fraction. Table 3 shows values of P and film thickness of those PVA fractions. The dawability of these fractionated PVA films at

Table 3. Degree of polymerization of fractionated PVA and film thickness.

Degree of polymerization	750	1020	1270	1500	1910	3550
Film thickness (μ)	18.2	14.8	15.6	15.7	15.6	15.7

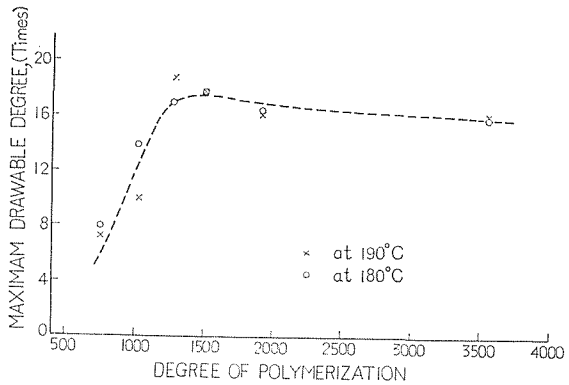

Fig. 1. The relation between the degree of polymerization of the fractionated PVA and the maximum drawable degree at elevated temperature.

180°C and 190°C is shown in Fig. 1, and the tensile strength and elongation of films stretched 10 times or to the maximum degree are shown in Table 4 and Table 5.

In Fig. 1 no difference can be seen between the results obtained at 180°C and 190°C, and drawability increases with P at first, then tends to decrease slightly after P reaches to a high value.

In Table 4 any significant difference can not be seen in tensile strength when P exceeds 1020 except for the case of $P=1910$. Extraordinay high ten-

Table 4. Tensile strength and elongation of fractionated PVA films stretched 10 times[a].

Degree of polymerization	750	1020	1270	1500	1910	3550
Tensile strength (kg/mm²)	39.4	87.2	78.0	76.0	112.8	81.2
Elongation (%)	10.2	15.0	13.2	10.1	17.5	13.1

[a] Stretched at 180°C.

Table 5. Tensile strength and elongation of fractionated PVA films stretched to maximum degree.

Degree of polymerization	750	1020	1270	1500	1910	3550
Stretching ratio[a]	8.0	13.0	16.5	17.0	16.0	15.5
Tensile strength (kg/mm²)	39.4	102.9	121.7	132.0	138.1	160.0
Elongation (%)	8.0	9.8	6.5	5.5	8.1	12.1

[a] Stretched at 180°C.

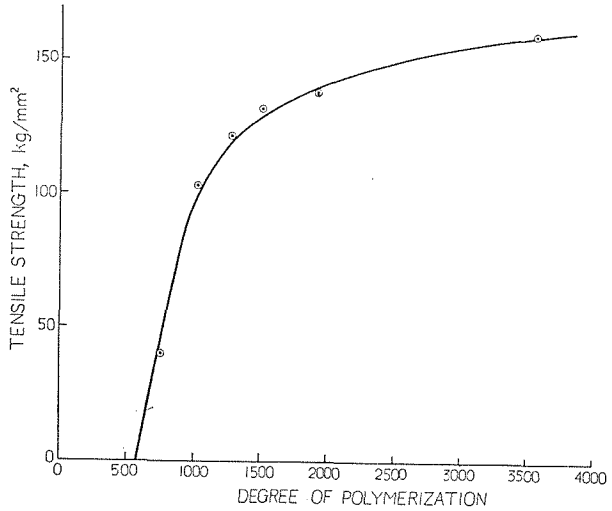

Fig. 2. The relation between the degree of polymerization of the fractionated PVA and the tensile strength of film heat-stretched to maximum degree.

sile strength was obtained at $P=1910$. Similar phenomenon was found some times in our work in the range of $P=1500\sim2000$. It might be attributed to the better molecular orientation but has not be examined in detail.

Systematic results of the effect of P on tensile strength can be seen when compared at maximum stretching. The values of tensile strength of the films stretched to maximum degree shown in Table 5 are plotted against P in Fig. 2. If these values of tensile strength are plotted against the reciprocal values of P a linear relationship is found as shown in Fig. 3 except in the case of $P=750$. Thus it is shown in this case that the following equa-

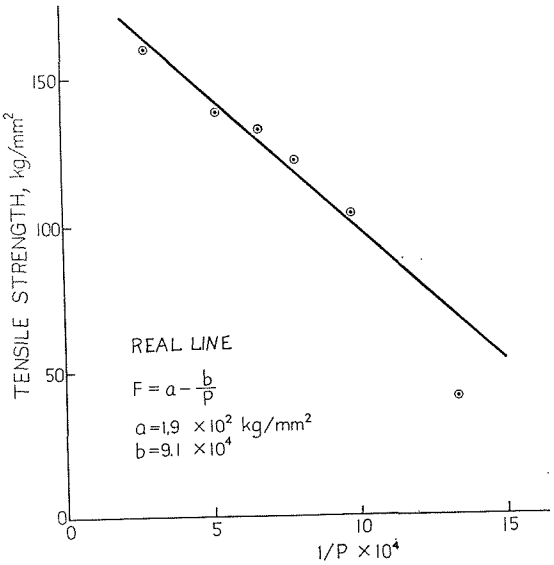

Fig. 3. The relation between the reciprocal of degree of polymerization of the fractionated PVA and the tensile strength of film heat-stretched to maximum degree.

tion represents the relation between tensile strength F (kg/mm²) and P. This corresponds to equation (1) described before.

$$F=a-b/P \qquad (2)$$
$$a=190 \text{ kg/mm}^2$$
$$b=9.1\times10^4 \text{ kg/mm}^2$$

From this relation it is shown that the maximum value of tensile strength which is expected for the case of $P=\infty$ would be $a=190$ kg/mm² (corresponds to 16.6 g/d), and that the tensile strength would be nearly zero for the value of P less than 480.

3.3. The Effect of the Heterogeneity of Molecular Weight

Several mixtures of PVA were prepared by blending two suitable fractions to obtain PVA samples which had same M_v but different M_n, and their mechanical properties were studied. Table 6 shows the degree of polymeri-

Table 6. PVA Blends with same P_v and different P_n.

Sample No.	Degree of polymerization of the fractions used to blending		Average degree of polymerization of the blends		Heterogeneity of P of the blends
	F_1	F_2	P_v*	P_n*	P_v/P_n
1	1540	—	1540	1540	1.0
2	1910	1020	1540	1430	1.1
3	3200	735	1540	825	1.9
4	3200	279	1540	540	2.9

* Calculated assuming that the degree of polymerization of fractionated PVA is homogeneous.

Table 7. The effect of heterogeneity of the molecular weight of PVA on tensile strength and elongation of film.

Sample No.	P_v	P_n	P_v/P_n	Film thickness (μ)	Tensile strength (kg/mm²) Stretching ratio				Elongation (%) Stretching ratio			
					1.0	2.0	3.0	4.0	1.0	2.0	3.0	4.0
1	1540	1540	1.0	12.3	10.0	23.4	41.2	65.8	30.2	25.8	17.4	16.5
2	1540	1430	1.1	11.5	9.8	26.3	45.3	80.9	25.4	23.3	18.3	15.9
3	1540	825	1.9	13.3	10.4	18.8	32.7	42.6	29.8	29.4	23.1	18.3
4	1540	540	2.9	11.9	10.9	23.0	34.6	54.6	26.3	25.4	21.0	16.3
Commercial PVA (unfractionated)	1540	—	—	10.6	9.7	18.5	28.3	49.5	28.5	22.9	24.0	18.1

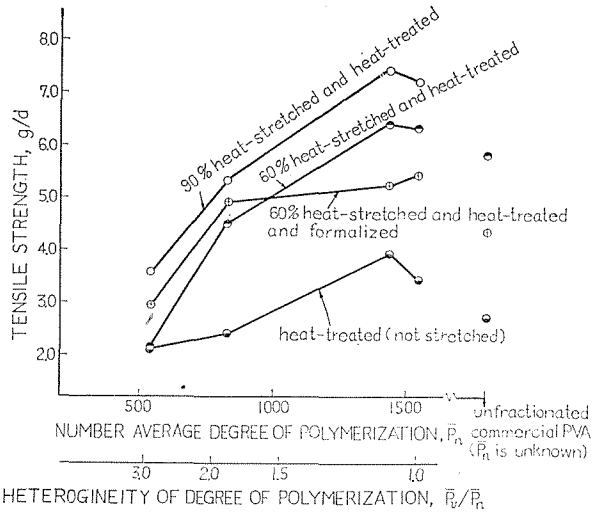

Fig. 4. The relation between the heterogeneity of degree of polymerization (P_n or P_v/P_n) and the tensile strength of PVA fiber (all PVA have same viscosity average degree of polymerization, 1540).

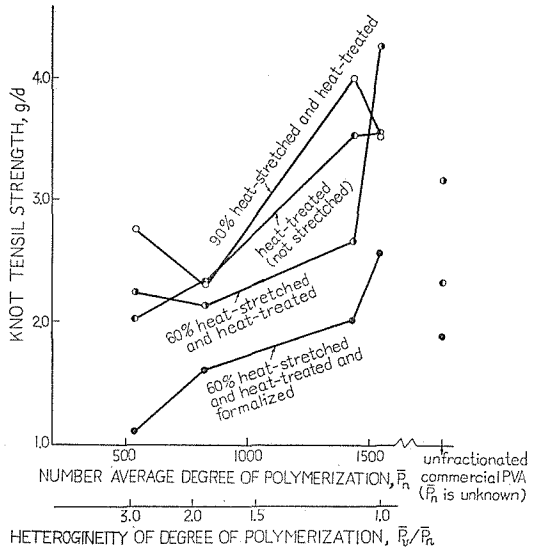

Fig. 5. The relation between the heterogeneity of degree of polymerization (P_n or P_v/P_n) and the knot tensile strength of PVA fiber (all PVA have same viscosity average degree of polymerization).

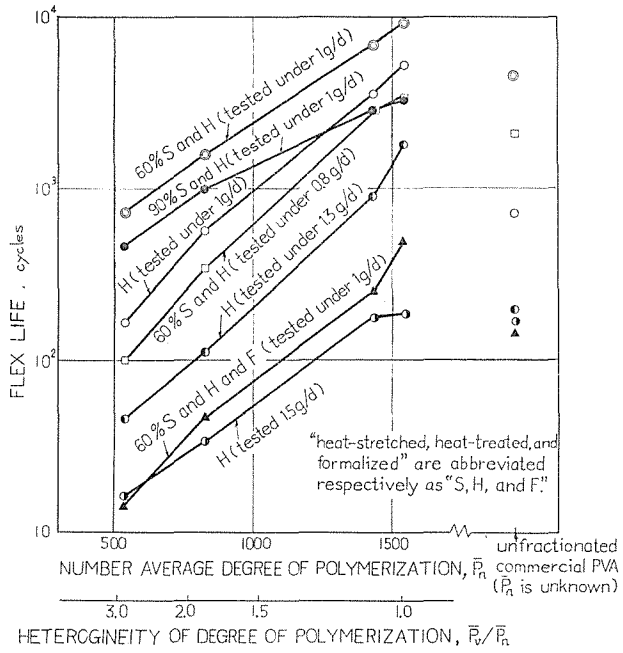

Fig. 6. The relation betweem the heterogeneity of degree of polymerization (P_n or P_v/P_n) and the flex strength of PVA fiber (all PVA have same viscosity average degree of polymerizatino, 1540).

zation and its heterogeneity of the blends used. The tensile strength and elongation of the heat stretched films of various PVA blends described in Table 6 are shown in Table 7.

Though the effect of P_n or P_v/P_n is not clear at low degree of stretching, an effect is obviously found at high degree of stretching. The effect of P_n or P_v/P_n on elongations was rather small.

Next, the mechanical properties of fibers prepared by usual method were studied by using the same PVA blends. In Fig. 4, 5 and 6, the values of tensile strength, knot-strength and flex strength of fibers of various PVA blends described in Table 6 are plotted against P_n and heterogeneity of P $(=P_v/P_n)$. It is shown that these properties generally increase with increasing P_n. The effect is most remarkable in flex fatigue. The effect on elongation is not clear also in this case.

Further, the effect of heterogeneity of P on some other properties are shown in Table 8. It appears that wet strength decreases more sensitively

Table 8. The effect of heterogeneity of the molecular weight on some properties of PVA fibers.
(60 % stretched, heat treated and formalized fibers)

Sample No.	P_v	P_n	P_v/P_n	Denier (d)	Wet tensile strength (g/d)	Young's modulus (kg/mm²) Dry	Young's modulus (kg/mm²) Wet	Elastic recorvery (%) At 3% elongation	Elastic recorvery (%) At 5% elongation
1	1540	1540	1.0	1.05	5.15	1084	449	77	61
2	1540	1430	1.1	1.24	4.71	1304	531	77	65
3	1540	825	1.9	1.30	4.02	1120	515	77	67
4*	1540	540	2.9	1.26	1.93	706	186	73	61

* 50 % stretched.

with increasing of heterogeneity of P than dry strength does. The effect is not obvious in elastic modulus except the most heterogeneous case.

3.4. The Effect of the Degree of Conversion in VAc Polymerization

Generally PVA is prepared by the saponification of PVAc, so its homogeneity of molecular weight may be affected by the degree of monomer conversion in VAc polymerization. It is considered that the homogeneity of molecular weight of PVA may be lowered due to chain branching of PVAc when the conversion in VAc polymerization becomes high. So the mechanical properties of PVA samples which have been prepared by the saponification of PVAc polymerized with different degree of conversion of VAc were studied.

Preparation of PVA. Some samples of PVAc were prepared by solution polymerization of VAc with azobisisobutylonitrile (ABIN) as initiator and ethylacetate as solvent, and were saponified by alkali in usual way. PVA, thus obtained, were resaponified till its acetyl residues decreased below 0.1 mole %. Table 9 shows the polymerization condition, degree of conversion of VAc and P_v of PVAc and PVA thus obtained. These PVA samples have some different degree of polymerization, but the difference is not so large that it has remarkable effect on mechanical properties.

Table 9. Synthesis of PVA with different degree of conversion in VAc polymerization.

Sample No.	Composition		Polymerization time (min.)*	Conversion of VAc (%)	P_v of PVAc	P_v of PVA
I-1	VAc	200 g	45	20.7	1520	1460
I-2	Ethyl Acetate	100 g	65	41.1	1810	1500
I-3	ABIN	0.5 g	90	64.0	2200	1220
I-4			250	99.2	2880	1020
II-1	VAc	200 g	80	65.8	2510	1585
	Ethyl Acetate	50 g				
II-2	ABIN	0.5 g	250	97.0	3170	1395

* Temperature of polymerization : 70°C.

Table 10. Heat prawability of the PVA films prepared from PVAc with different VAc conversions.

Sample No.	VAc Conversion (%)	P_v of PVA	Film thickness (μ)	Maximum drawable degree (Times) Drawing temperature (°C)			
				170	180	190	200
I-1	20.7	1460	18.4	17.3	18.2	17.8	12.2
I-2	41.1	1500	19.7	15.5	17.6	16.8	11.3
I-3	64.0	1220	18.5	17.0	14.6	15.5	9.3
I-4	99.2	1020	20.2	16.1	13.7	9.5	8.5
II-1	65.8	1585	18.9	16.3	17.0	15.2	14.2
II-2	97.0	1395	15.8	12.8	14.8	13.2	9.1
Commercial PVA	(~100)	1500	18.2	13.6	14.5	14.7	12.3

Table 11. Tensile strength and elongation of the PVA films prepared from PVAc with different VAc conversions.

Sample No.	VAc Conversion (%)	P_v of PVA	No Stretching film		10 Times stretched film*		Maximum stretched film*		
			Tensile strength (kg/mm²)	Elongation (%)	Tensile strength (kg/mm²)	Elongation (%)	Stretched degree (times)	Tensile strength (kg/mm²)	Elongation (%)
I-1	20.7	1460	7.7	195	135	18.7	17.0	167	22.5
I-2	41.1	1500	7.8	278	105	13.0	16.0	144	19.2
I-3	64.0	1220	6.8	277	86	11.9	14.0	113	19.5
I-4	99.2	1020	4.9	138	75	8.0	13.0	77	14.8
II-1	65.8	1585	3.8	264	75	18.4	16.0	106	15.5
II-2	97.0	1395	3.5	184	66	12.5	14.0	101	8.6
Commercial PVA	(~100)	1500	4.3	194	54	12.1	13.0	69	8.6

* Stretched at 180°C.

Mechanical properties of PVA films prepared from PVAc with different VAc conversion. Maximum heat drawability of PVA films shown in Table 9 was measured. The results obtained are shown in Table 10. It seems that somewhat higher maximum drawability is generally obtained at lower VAc conversion.

The tensile strength and elongation of these films are shown in Table 11. It is seen that the tensile strength generally decreases with increasing VAc conversion. The effect is more remarkable at higher stretching.

It is supposed that this effect of VAc conversion on the mechanical property of PVA film probably comes from the heterogeneity in molecular weight. The wider distribution of molecular weight was observed by Spencer's method (using acetone as a solvent and acetone-water as a precipitant) for PVAc which was prepared by the reacetylation of PVA obtained from PVAc of the higher VAc conversion.

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ERRATUM

The experimental points by □ *in Fig. 6 are 60% S and H and F (tested under 0.8 g/d).*